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Measuring Conductivities of Highly Conductive Membranes

by

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Measuring Conductivities of Highly Conductive Membranes

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Abstract

The theoretical and experimental aspects of an electrochemical approach for evaluating the conductivities of highly conductive membranes are described. The methods developed involve either a current or a potential step at a solid-state electrochemical cell. It is assumed, and we prove, that only capacitive currents flow during these current or potential step experiments. The theory for these methods is derived from classical electrochemical theory for current and potential steps at RC circuits. We show that if the conductivity of the system under study is not too high (less than ca. $0.2 \text{ ohm}^{-1} \text{ m}^{-1}$), the classical theory provides accurate conductivity data. However, we also show that if the conductivity of the system is greater than ca. $0.2 \text{ ohm}^{-1} \text{ m}^{-1}$, conductivities obtained from the classical expressions are inaccurate. The modified theoretical analysis developed here, however, yields very accurate conductivity data for such highly conductive systems. The modifications of the classical theory entail accounting for the non ideal wave shape of real potential or current step waveforms.



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INTRODUCTION.

Investigations of the conductivities of biological (1,2) and artificial (3-5) membranes are of great theoretical and practical importance. A number of electrochemical methods for evaluating the conductivities of such membranes have been developed (6-12). These methods have a number of well documented limitations, particularly with regard to the measurement of membranes with inherently high ionic conductivities (11,12).

We are investigating new, highly conductive, ion-transporting membranes (13,14). Because of the shortcomings of existing methods, we have developed two new electrochemical procedures for measuring the conductivities of these membranes. The theory for these methods is derived from classical theory for current and potential steps at RC circuits (15). We show here that if the conductivity of the system under study is less than ca. $0.2 \text{ ohm}^{-1} \text{ m}^{-1}$, analysis of experimental data via classical theory yields accurate conductivity values. However, if the conductivity of the system is greater than ca. $0.2 \text{ ohm}^{-1} \text{ m}^{-1}$, classical theory yields inaccurate conductivity data.

The classical theoretical analysis is not applicable to highly conductive membranes because it does not account for the nonideal nature of the current or potential "step" waveforms put out by real potentiostats and galvanostats (See Figures 1a and 2a). The methods and modified theoretical analyses developed here account for these nonidealities. We show that when experimental data are analyzed via the modified theory, accurate conductivity data are obtained for highly conductive systems.

EXPERIMENTAL SECTION.

Electrochemical Cell. A solid state electrochemical cell, similar to the cell designed by Nedyalkov and Gavach (8), was used for all measurements. Electrodes were prepared by heat sealing (16) graphite rods (dia = 1 cm) into machined Kel-F bodies (dia. = 2 cm). The rod and surrounding Kel-F were then sanded flat with 600 grit silicon carbide paper. The cell was assembled by sandwiching the membrane to be studied between two such graphite rod working electrodes. Pressure was applied across the cell by placing a column of Hg on the upper half cell. Unless otherwise noted, a pressure of 150 g cm^{-1} was used. The temperature of the cell was maintained at 25°C by immersion in a thermostated water bath.

In order to test the accuracy of the methods developed here, solutions of known conductivities were also investigated. When solutions were used in the electrochemical cell, a washer of known thickness and inner diameter was applied to the surface of the lower half cell. The washer was filled with the solution to be studied and the upper half cell was applied.

Instrumentation and Equipment. Electrochemical measurements were accomplished using an EG&G PAR 173 potentiostat/galvanostat in conjunction with a PAR 175 programmer and a Nicolet 2090 digital oscilloscope. In order to minimize the possibility of contamination of the membrane by faradaic processes, the duration of the current and potential steps were kept very short (less than or equal to 1 ms). Data were analyzed with the help of the spread sheet Lotus 1-2-3 (Lotus Development Corporation).

Materials and Reagents. Nafion^R perfluorosulfonate ionomer membrane (1150 equivalent weight) was obtained from Du Pont. Composite membranes were prepared by impregnating a microporous polytetrafluoroethylene host membrane

(Gore-Tex) with Nafion (13,14). Impregnation was accomplished by immersing the host membrane into a Nafion solution and evaporating the solution to dryness (13,14). Two types of Nafion-impregnated Gore-Tex (NIGT) membranes were prepared; the first (designated NIGT-RT) were prepared by evaporating the solution to dryness at room temperature as per (13). The second type of NIGT membrane (designated NIGT-HT) was prepared by evaporating the solution to dryness at 185° C as per reference (17). All composite membranes contained 10 % Nafion by weight.

THEORY.

The major difference between the classical theories (15) and the theories developed here lies in the shape of the potential or current wave form. In the classical theories, it is assumed that an ideal current or potential step is applied to the cell; (i.e. current or potential rises from zero and instantaneously achieves the desired final value). Potential or current steps obtained from real potentiostats or galvanostats do not achieve this ideal shape. For example, wave forms obtained with the PAR instrumentation are shown in Figures 1a and 2a. The theories developed below take into account the effects of these nonideal waveforms on the measured membrane (or solution) conductivity.

We assume that the cell contains ideal polarizable electrodes. Thus, the cell can be approximated by an equivalent circuit consisting of a series combination of a capacitor (C_1), a resistor (R), and a second capacitor (C_2). The capacitors represent the double layer capacitances of the two membrane/electrode interfaces. We assume that the capacities of C_1 and C_2 do not change during the course of the experiment. The experimental data show that this assumption is valid (see below).

The resistance, R , is the sum of the membrane resistance, R_m (which is the parameter we want to measure), and the instrumental resistance, R_i . R_i includes the metal-carbon and metal-metal contact resistances, the wire resistances, and the output resistance of the instrument. These resistances cannot be ignored when highly conductive systems are being investigated.

Current Step Method. Figure 3a represents the cell when no potential is applied and no current is flowing. The initial (rest) potential difference (E_0) is given by

$$E_0 = q_{10}/C_{d1} - q_{20}/C_{d2} \quad (1)$$

where q_{10} and q_{20} are the charges residing on C_1 and C_2 . The current source in Figure 3a produces some unspecified waveform such that at any time, t , the current is i_t . The polarity of the current source is such that when the switch is closed, electrons circulate counter clockwise through the circuit; the polarity is never reversed.

The switch is closed at time $t = 0$; Figure 3b shows the situation after some relatively brief time $t=t_1$. The charges at each interface are now given by

$$q_1 = q_{10} + \int_{t=0}^{t=t_1} i_t dt \quad (2)$$

$$q_2 = q_{20} - \int_{t=0}^{t=t_1} i_t dt \quad (3)$$

The total potential difference across the cell at $t=t_1$ is

$$E_1 = i_{t1}R + q_1/C_{d1} - q_2/C_{d2} \quad (4)$$

Substituting Equations 1, 2 and 3 into Equation 4 and rearranging gives

$$E_1 = E_0 + i_{t1}R + \int_{t=0}^{t=t_1} i_t dt / C_d \quad (5)$$

where C_d is defined as

$$C_d = \frac{C_{d1} + C_{d2}}{C_{d2}C_{d1}} \quad (6)$$

Equation 5 describes the variation in cell potential when a current of unspecified character flows through the cell. This equation can now be tailored to the real current waveform (Figure 1a). The real waveform rises gradually (rather than instantaneously) from $i=0$ to the desired applied current (i_s) (Figure 1a). The time at which i_s achieved is defined as t_s . The duration of the electrochemical experiment (t) is always greater than t_s ; thus, the total charge passed during the experiment is given by

$$\int_{t=0}^{t=t} i_t dt = \int_{t=0}^{t=t_s} i_t dt + i_s(t - t_s) \quad (7)$$

Substituting Equation 7 into Equation 5 gives the following expression for the variation of E with t upon application of the real current waveform (Figure 1a) to the electrochemical cell.

$$E = E_0 + i_s R + \frac{\int_{t=0}^{t=t_s} i_t dt - i_s t_s}{C_d} + \frac{i_s}{C_d} t \quad (8)$$

Equation 8 indicates that a plot of E vs. t (for times greater than t_s) should be linear. Both t_s and the integral in Equation 8 can be obtained from the current waveform (Figure 1a). Thus, C_d can be obtained from the

slope of the E vs. t plot and R can be obtained from the intercept. Recall that $R = R_m + R_i$. R_i can be evaluated by conducting a current step experiment with no membrane present in the cell and the graphite rods in contact. With R and R_i known, R_m can be calculated.

If the current pulse is assumed to be ideal (i.e. the current raises instantaneously to i_s), Equation 8 can be simplified to

$$E = E_o + i_s R + \frac{i_s t}{C_d} \quad (9)$$

Equation 9 is analogous to the classical expression for the E vs. t transient following an ideal current step at an RC circuit (15). Equation 9 also predicts that E varies linearly with t. In this case, however, it is much easier to obtain R.

Potential Step Method. Figure 2b shows a typical current-time transient for a Nafion membrane; a rounded maximum is observed ca. 10 μ s after application of the potential "step." For a given membrane, the time required to reach this maximum (t_m) is highly reproducible. R will be calculated from this current maximum.

If E_m is the potential at which the current maximum (i_m) occurs, Equation 5 can be rewritten as

$$E_m - E_o = i_m R + \int_{t=0}^{t=t_m} i dt / C_d \quad (10)$$

Let I represent the integral in Equation 10. For reasons which will become apparent below, Equation 10 is rearranged to

$$R = \frac{E_m - E_o}{[i_m + (I/RC_d)]} \quad (11)$$

E_m and E_o can be obtained from the experimental potential-time waveform (Figure 2a); I and i_m can be obtained from the experimental current-time transient (Figure 2b). Thus, if the product RC_d can be evaluated, Equation 11 can be used to calculate R .

At long times, the real potential-time waveform achieves a constant value E_s , the applied potential (Figure 2a). Since E is now invariant with time, differentiation of Equation 5 yields

$$R(di/dt) + i/C_d = 0 \quad (12)$$

Solving Equation 12 for i gives (18)

$$\ln i = B - t/RC_d \quad (13)$$

where B is an integration constant. Equation 13 indicates that the product RC_d can be obtained from a plot of $\ln i$ vs. t (Figure 4); this product can then be used with Equation 11 to calculate R .

If the potential step waveform was ideal, the resulting i - t transient would be given by the classical expression (15,18)

$$\ln i = \ln(E_a - E_o)/R - t/RC_d \quad (14)$$

where E_a is the applied potential. R could be obtained directly from a plot of $\ln i$ vs. t .

Conductivities were calculated from the R_m data via

$$S = d/R_mA \quad (15)$$

where S is the conductivity ($\text{ohm}^{-1} \text{ cm}^{-1}$), and d and A are the thickness and area (respectively) of the membrane or solution layer in the cell. Finally, we have compared solution conductivities calculated via the exact expression (Equation 11) with conductivities calculated via the classical expression (Equation 14). As we shall see, when solution conductivities are high, the classical expression yields substantial errors.

RESULTS AND DISCUSSION.

General Electrochemical Characteristics. Figure 1b shows a typical E vs. t transient for a Nafion film. The nonideal nature of the applied current waveform (Figure 1a) is manifested as the nonlinear E vs. t response observed at short times (Figure 1b). This nonlinearity is not predicted by the classical expression (Equation 9). At longer times E varies linearly with t , as predicted by our Equation 8. As noted above, both R and C_d can be obtained from the linear region in Figure 1b.

Figure 2b shows a typical i vs. t transient for a Nafion film. The nonideal nature of the applied potential waveform (Figure 2a) is manifested as the gradual rise of the current to a broad maximum (Figure 2b). A typical plot of $\ln i$ vs. t for the longer time data is shown in Figure 4. The product RC_d can be obtained from the slope of this plot; RC_d can be used in conjunction with Equation 11 to obtain R .

The data in Figures 1b, 2b and 4 indicate that the theoretical models developed here are correct. Furthermore, the linearity of the E vs. t (Figure 1b) and $\ln i$ vs. t (Figure 4) plots indicates that C_d remains constant throughout the duration of these experiments.

Contact Resistance. An important question has yet to be addressed - how do we know that a layer of solution does not separate the membrane from the electrode surface. Or, given the fact that these surfaces are not atomically smooth, - how do we know that isolated layers of solution do not collect in surface depressions, again, separating the membrane from the electrode surface. In fact, we cannot be certain that such solution layers do not exist. We can, however, demonstrate that such layers, if they do exist, are so thin that they do not affect the measured resistance.

Figure 5 shows the effect of applied pressure on the measured membrane resistance; R_m initially decreases with applied pressure but becomes pressure independent at pressures above 100 g cm^{-2} . The initial decrease in resistance with pressure results from improved contact between the membrane and the electrodes. This improved contact probably entails expulsion of solution layers which initially separate the membrane from the electrode. At high pressures, these solution layers have either been completely eliminated or have become so thin that their resistances are insignificant compared to the resistance of the membrane.

The above discussion suggests that if modest pressures (Figure 5) are applied to the cell, the contact resistance is negligible. This point can be further reinforced through an investigation of the resistances of stacks of membranes. If the contact resistance is negligible, a plot of the resistance of the stack vs. the number of membranes in the stack should be linear and pass through the origin. If the contact resistance is not negligible this plot will have an intercept equivalent to the contact resistance. Figure 6 summarizes the results of such an experiment; the linearity (correlation coefficient = 0.997) and negligible intercept (0.073 ohms) clearly indicate that the contact resistance is insignificant.

Effect of Other Experimental Parameters. We assume that only capacitive currents flow during the course of these experiments. The validity of this assumption can be tested by evaluating the effect of the upper limit of the potential step on the measured resistance (Figure 7). Resistance is independent of step height until steps of ca. 2 V are applied. This observation is in concordance with the capacitive model in that faradaic currents are not possible until the potential difference between the

electrodes is sufficient to electrolyze water; this is not possible until potential differences of ca. 2 V or larger are applied to the cell (19).

When steps of 2 volts or higher are applied, some fraction of the total current is faradaic and the purely capacitive model is no longer applicable. This is signaled by a potential-dependent R . The increase in R at high potential (Figure 7) may be due to gas evolution (induced by the faradaic current) at the membrane/electrode interfaces.

Figure 8 shows the effect of step height on membrane resistances measured via the current step method. Note, first, that the current step method is much less precise than the potential step method (compare error bars in Figures 7 and 8; error bars in all figures represent twice the standard deviation of replicate measurements). The lower precision of the current step method may be caused by the abbreviated linear response range in the plot of E vs. t (Figure 1b) and the low values of the intercepts obtained for highly conductive systems (generally less than 10 mV).

In spite of the relatively large error bars in Figure 8, it is clear that the measured resistance slowly decreases as the magnitude of the current step increases. A current step height of 5 mA was used in the studies to be reported below.

Determinations of Solution and Membrane Conductivities Using These Methods.

Table I compares specific conductances determined using the current step and potential step methods with analogous conductance values obtained from the literature (20-22). Note that the current step and potential step methods yielded identical results for all systems studied; again, the current step method is less precise than the potential step method.

Solution conductances measured using the methods developed here are, within experimental error, identical to the values obtained from the literature (Table I). It is difficult to compare measured and literature values for Nafion membranes because conductivity is highly dependent on solvent content and thermal history (vide infra). However, the membranes in Table I were subjected to the same pretreatment procedure as the membranes in the literature citation (22); the agreement between the value obtained here and the literature value is quite good.

The remaining studies were conducted using the, more precise, potential step method. Table II compares specific conductances calculated from our exact expression (Equation 11) and from the classical expression (Equation 14) with conductance data obtained from the literature (20,21). For the relatively low conductivity systems (S less than ca. $1 \text{ ohm}^{-1} \text{ m}^{-1}$), the exact and approximate expressions give essentially identical results; furthermore, these results agree with the literature conductivities.

In contrast, the exact and approximate expressions yield significantly different values of S for the highly conductive systems. Furthermore, the exact expression (Equation 11) yields S 's which are in agreement with the literature data, whereas the classical expression (Equation 14) yields smaller values (Table II). These data clearly point out the importance of the new potential step method, developed here, for measuring conductivities of highly conductive membranes.

Table III shows the effect of salt content in a contacting electrolyte phase on conductivity in Nafion. As-received Nafion membrane (proton form) was boiled for 30 min. in water and then equilibrated for at least 6 hours

in the indicated NaCl solution. The membrane conductivity was then measured using the potential step method. The data were analyzed via Equation 11.

When Nafion is equilibrated with relatively low concentrations of electrolyte, excess salt is excluded from the membrane phase and the conductivity is independent of external salt concentration (Table III). However, at high external salt concentrations, Donnan exclusion breaks down (23) and excess electrolyte enters the membrane phase. This excess electrolyte causes the conductivity of the membrane to increase (Table III).

According to Donnan theory, the equilibrium NaCl concentrations in the membrane and solution phases are related via (23)

$$[\text{Na}^+]_m [\text{Cl}^-]_m = [\text{Na}^+]_s [\text{Cl}^-]_s \quad (16)$$

where the subscripts "m" and "s" refer to the membrane and solution phases, respectively; activity effects have been ignored. Furthermore, electroneutrality requires that

$$[\text{Na}^+]_m = [-\text{SO}_3^-]_m + [\text{Cl}^-]_m \quad (17)$$

where $-\text{SO}_3^-$ represents the fixed sulfonate sites in the Nafion membrane. Equations 16 and 17 can be used to calculate the $[\text{Cl}^-]_m$ in a Nafion membrane for any value of external salt concentration. This calculation requires a value for $[-\text{SO}_3^-]_m$; from the equivalent weight and the known water content of the membrane (31 percent by weight (22)), we calculate $[\text{SO}_3^-]_m = 2.7 \text{ M}$.

The values of $[\text{Cl}^-]_m$ obtained from Equations 16 and 17 can be used to compare experimental (Table III) and calculated conductivities for these membranes. We assume that the conductivity of the membrane which has been exposed to only pure H_2O is given by

$$S_0 = K[-\text{SO}_3^-] \quad (18)$$

while the conductivity, S , for a membrane after exposure to an NaCl solution is given by (24)

$$S = K([SO_3^-] + 2[Cl^-]_m) \quad (19)$$

where K is a proportionality constant. Equations 18 and 19 allow us to calculate the ratio S/S_0 which can be compared to the experimental ratio.

Figure 9 shows the results of this comparison. The calculated (solid) curve clearly shows the region of Donnan exclusion breakdown at high solution salt-contents. Before this exclusion breakdown region, the agreement between the calculated and experimental data is reasonably good, given the approximate nature of the calculations. However, the experimental data do not show the dramatic increase in conductivity associated with Donnan exclusion breakdown. This observation is in accord with prior evaluations of the permselectivity of Nafion membrane (25). Our conductivity data, then, are in agreement with the previous assessment that Nafion, shows higher permselectivity than would be predicted purely on the basis of Donnan theory.

Finally, Table IV compares specific conductances for Nafion and NIGT membranes after identical pretreatment procedures. The NIGT membranes have lower specific conductances than the Nafion membrane. Electron micrographs show that the Nafion in NIGT is dispersed throughout the Gore-Tex pore structure (13,14). Furthermore, while virgin Gore-Tex is hydrophobic, the pores in NIGT become flooded when the membrane is immersed in water (13,14).

The highly dispersed nature of the Nafion and the high membrane water contents suggest that the concentration of charge carriers (protons) within NIGT might be lower than in the conventional Nafion membrane. This conclusion is supported by the fact that NIGT is less cation permselective

than Nafion (14). This lower charge carrier concentration undoubtedly accounts for the lower specific conductance of the NIGT membrane (Table IV).

CONCLUSIONS

We have described the experimental and theoretical aspects of two modified electrochemical methods for evaluating the conductivities of highly conductive membranes. These procedures are derivatives of classical current and potential step methods but are based on exact, rather than approximate, mathematical expressions. We have shown that the potential step method is more precise and, for this reason, the potential step procedure is the method of choice. Finally, we have shown that this new potential step method produces accurate results for highly conductive systems whereas the classical (approximate) treatment of the step data yields inaccurate conductivity data.

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Table I. Comparison of Specific Conductances Obtained Using the Current Step and Potential Step Methods with Analogous Conductances Taken from the Literature

System Studied (ref.)	Specific Conductances (ohm ⁻¹ m ⁻¹)		
	Potential Step ^{a,b}	Current Step ^{a,c}	Literature
0.02 M NaCl	0.225 + 0.004	---	0.231 (21)
0.1 M NaCl	1.02 + 0.02	1.10 + 0.04	1.067 (21)
0.5 M NaCl	2.54 + 0.01	---	2.54 (21)
Nafion Membrane ^d	1.40 + 0.01	1.35 + 0.05	1.25 (22)

^a Each entry represents an average of 6 determinations standard deviations as shown.

^b Step Height = 0.1V; duration = 1 ms.

^c Step Height = 5 mA; duration = 1 ms.

^d As-received proton-form membrane was boiled for 30 min. in water prior to measurement.

Table II. Comparison of Specific Conductances from Potential Step Experiment (Calculated Using Exact^a and Classical^b Equations) with Conductances Obtained from the Literature

System Studied	Specific Conductance ^c (ohm ⁻¹ m ⁻¹)		Literature (20,21)
	Exact Equation ^a	Classical Equation ^b	
0.01 M NaCl ^f	0.101 + 0.001	0.101 + 0.001	0.102
0.02 M NaCl	0.225 + 0.004	0.218 + 0.005	0.231
0.05 M NaCl ^f	0.471 + 0.002	0.449 + 0.002	0.478
0.1 M NaCl	1.10 + 0.03	1.02 + 0.02	0.1067
0.25 M NaCl ^f	1.530 + 0.006	1.243 + 0.006	---
0.5 M NaCl ^f	2.54 + 0.01	1.86 + 0.01	2.545
1.0 M NaCl ^f	4.43 + 0.04	2.50 + 0.03	4.73
Nafion Membrane ^d	0.48 + 0.01	0.46 + 0.03	---
Nafion Membrane ^e	1.4 + 0.01	1.24 + 0.03	---

^a Equation 12

^b Equation 10

^c Each entry represents the average of 5 determinations.
Standard deviation as shown.

^d As-received Nafion membranes equilibrated in 25% NaCl aqueous solution overnight.

^e As-received Nafion membrane boiled in water in H⁺ form for 30 minutes and then equilibrated in 25% NaCl aqueous solution overnight.

^f Solution temperature is 18°C.

Table III. Specific Conductance of Nafion Membrane after Equilibration^a
with Various Aqueous NaCl Solutions.

Concentration of NaCl (M)	Conductivity of Membrane ($\text{ohm}^{-1}\text{m}^{-1}$)
0.0	0.88 + 0.01
0.0016	0.89 + 0.01
0.0080	0.90 + 0.01
0.0400	0.92 + 0.01
0.200	1.30 + 0.01
1.00	1.24 + 0.01
5.00	1.42 + 0.01

^a H^+ -form membranes were boiled in H_2O for 30 min. and then equilibrated for a least 6 hours with the indicated salt solution.

Table IV. Comparison of Conductivities of Nafion and Nafion-Impregnated Gore-Tex^a (NIGT) Membranes.

Membrane ^a	Thickness (mm)	Specific Conductances (ohm ⁻¹ m ⁻¹)
Nafion	0.20	1.40
NIGT-RT ^b	0.084	0.17
NIGT-HT ^c	0.084	0.21

^a All membranes were proton form and were pretreated by boiling in H₂O for 30 min. and equilibrating with 1.2 (w/w)% NaCl.

^b Room temperature cast NIGT membrane; see experimental section.

^c High temperature cast NIGT membrane; see experimental section.

Figure Captions

Figure 1 - (a) Typical (nonideal) current-time waveform applied by PAR Galvanostat to a Nafion membrane during a current step experiment. The sample was a 0.20 mm-thick H^+ -form Nafion.
(b) Potential vs. time transient resulting from the current waveform shown in Figure 1a.

Figure 2 - (a) Typical (nonideal) potential-time waveform applied by PAR Potentiostat to an NaCl solution during a potential step experiment. The sample was a 0.22 mm-thick layer of 0.1 M NaCl.
(b) Current vs. time transient resulting from the potential waveform shown in Figure 2a.

Figure 3 - Schematic representations of events occurring when a current waveform of unspecified characteristics is applied to the cell.
(a) Hypothetical circuit used to apply current waveform. Note that switch is open so that the system is at equilibrium.
(b) Situation after some brief time, t , following application of current waveform to the circuit. Note that current flow has caused the charge on C_2 to decrease and the charge on C_1 to increase (see text).

Figure 4 - Plot of $\ln(\text{current})$ vs. time for the data shown in Figure 2b.

Figure 5 - Effect of force applied to upper half cell on the measured resistance. Potential step method was used (step height and duration were 0.1 V and 0.5 msec, respectively). A 0.22 mm-thick Na^+ -form Nafion membrane was present in the cell.

Figure 6 - Effect of membrane thickness on measured membrane resistance. Thickness was varied by stacking 0.20 mm-thick Nafion membranes.

Figure 7 - Effect of the magnitude of the potential step on the measured membrane resistance. The sample was a 0.20 mm-thick Nafion membrane. The cell potential was stepped from 0.0 V to the values indicated in the Figure. Step duration was 0.5 msec.

Figure 8 - Effect of the magnitude of the current step on the measured membrane resistance. The sample was as per Figure 7. The current was stepped from 0 mA to the values indicated in the Figure. Step duration was 0.1 msec.

Figure 9 - Comparison of calculated and experimental conductivity ratios (see text) for a Nafion membrane after equilibration in the indicated NaCl solutions. (Points and line are calculated data; X's are experimental data). The membrane was 0.21 mm-thick and was pretreated by boiling in water for 30 min. followed by equilibration with the indicated NaCl solution for 6 hrs.

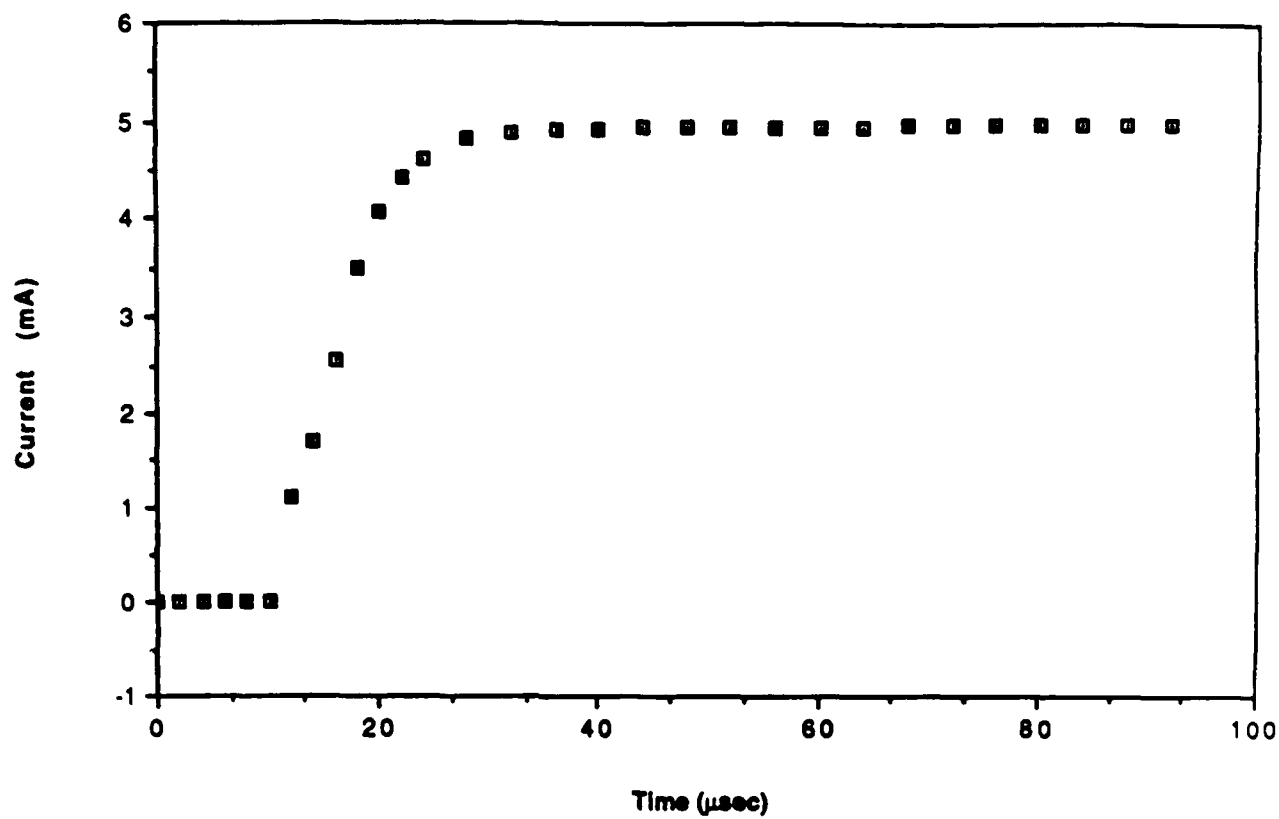


Fig. 1a

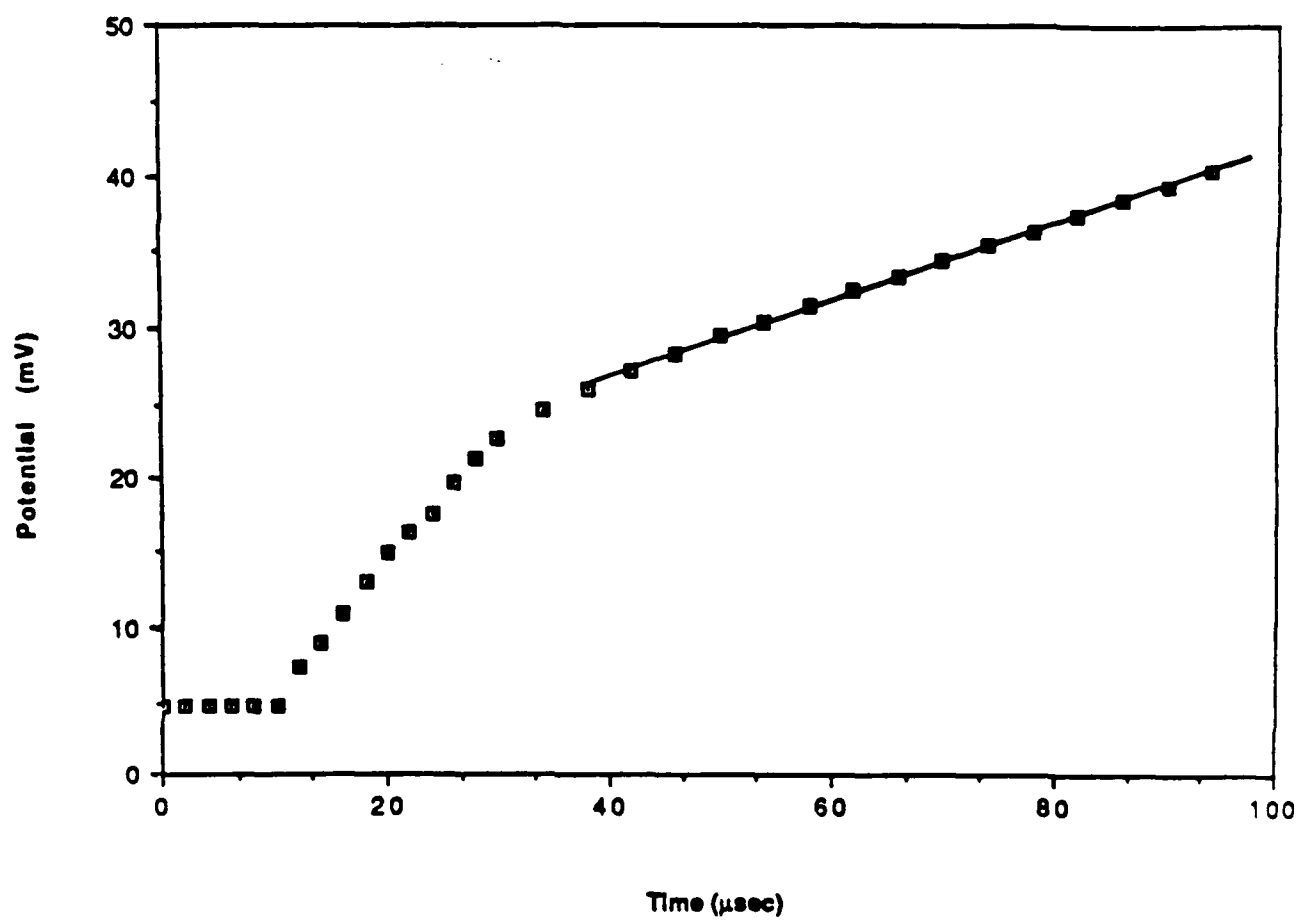


Fig 1b

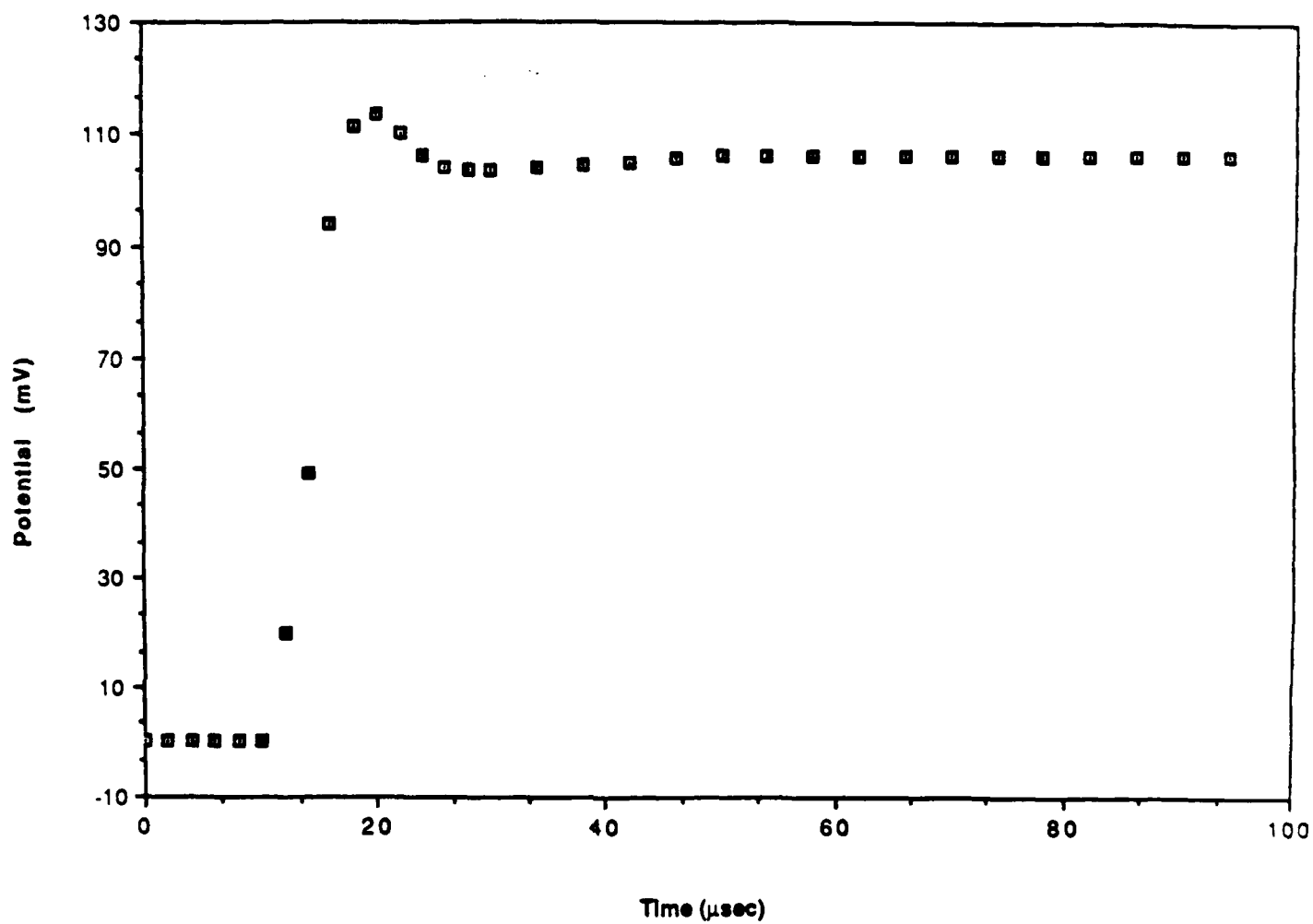


Fig. 2a

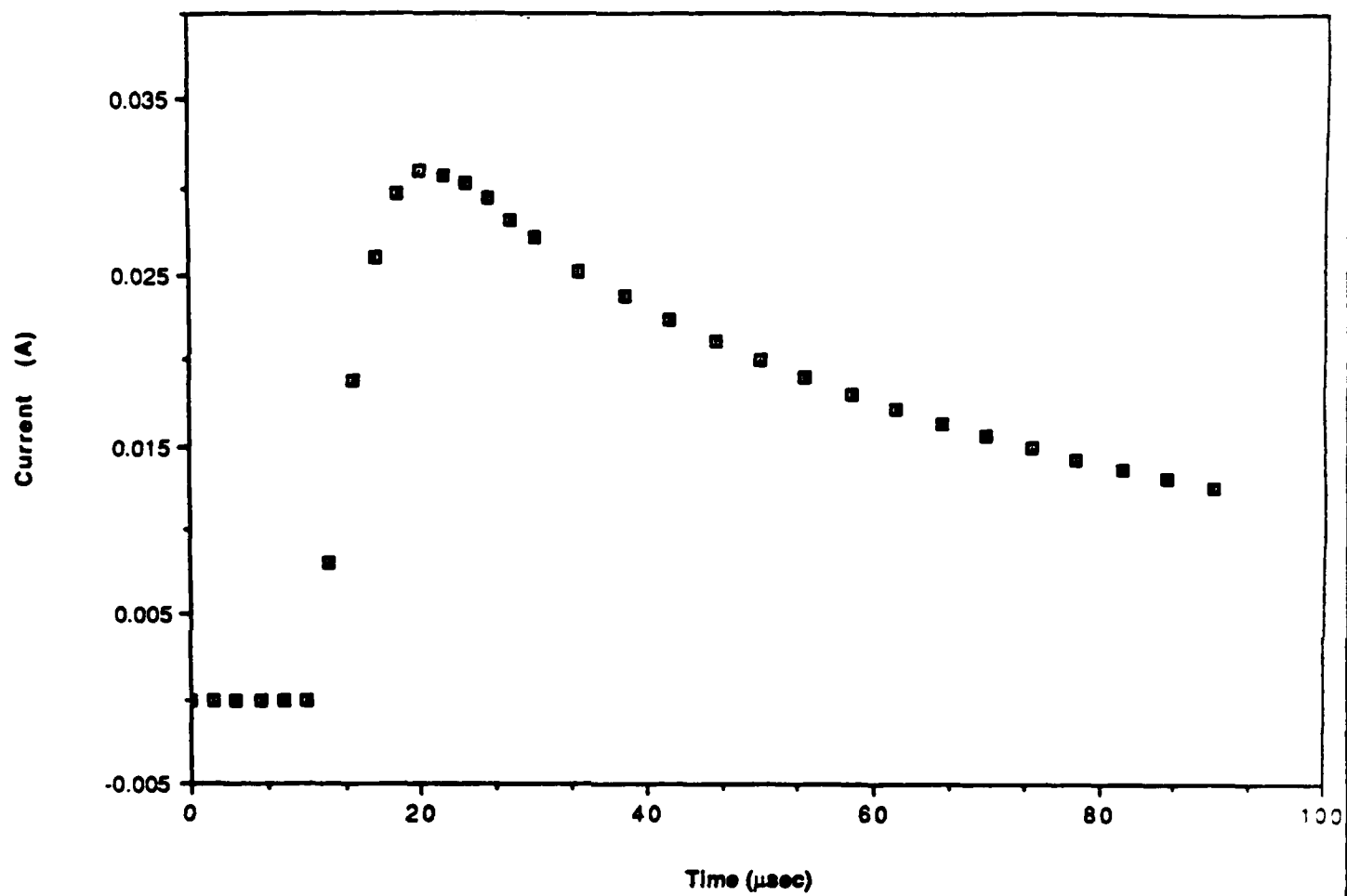


Fig 2.1

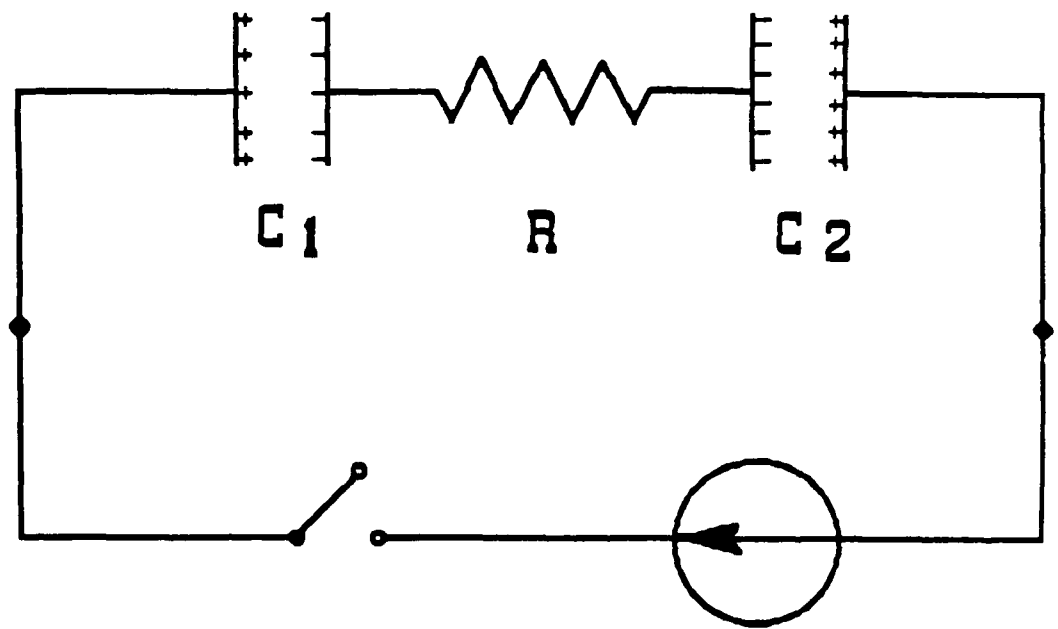


Fig. 3a

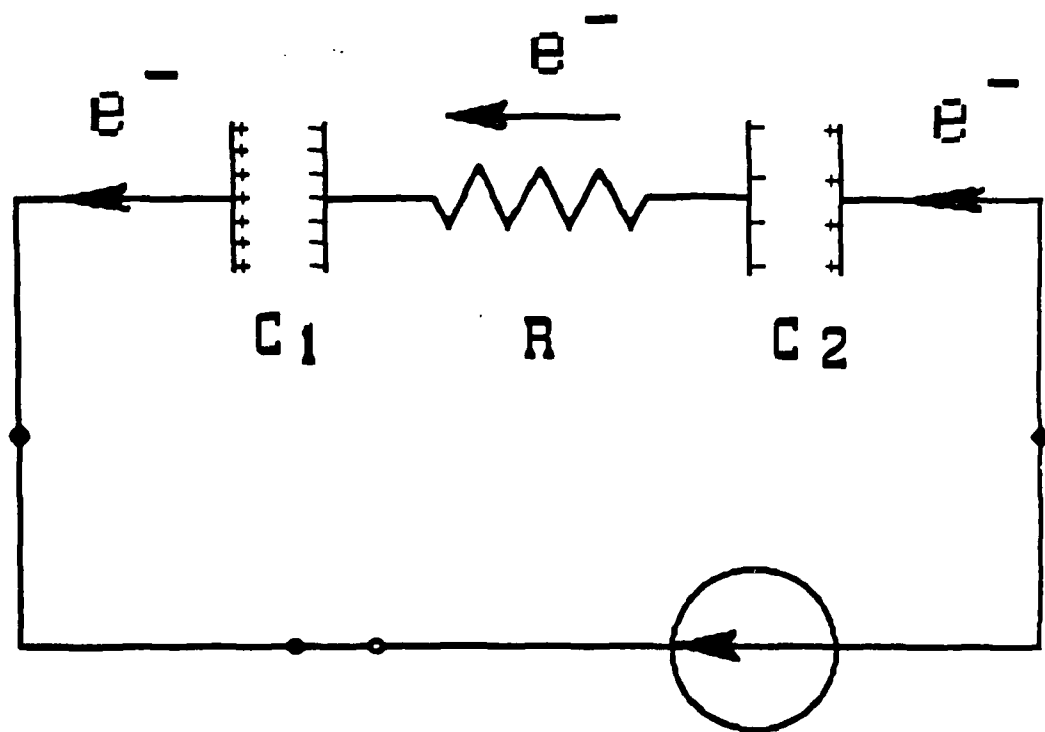


Fig 3b

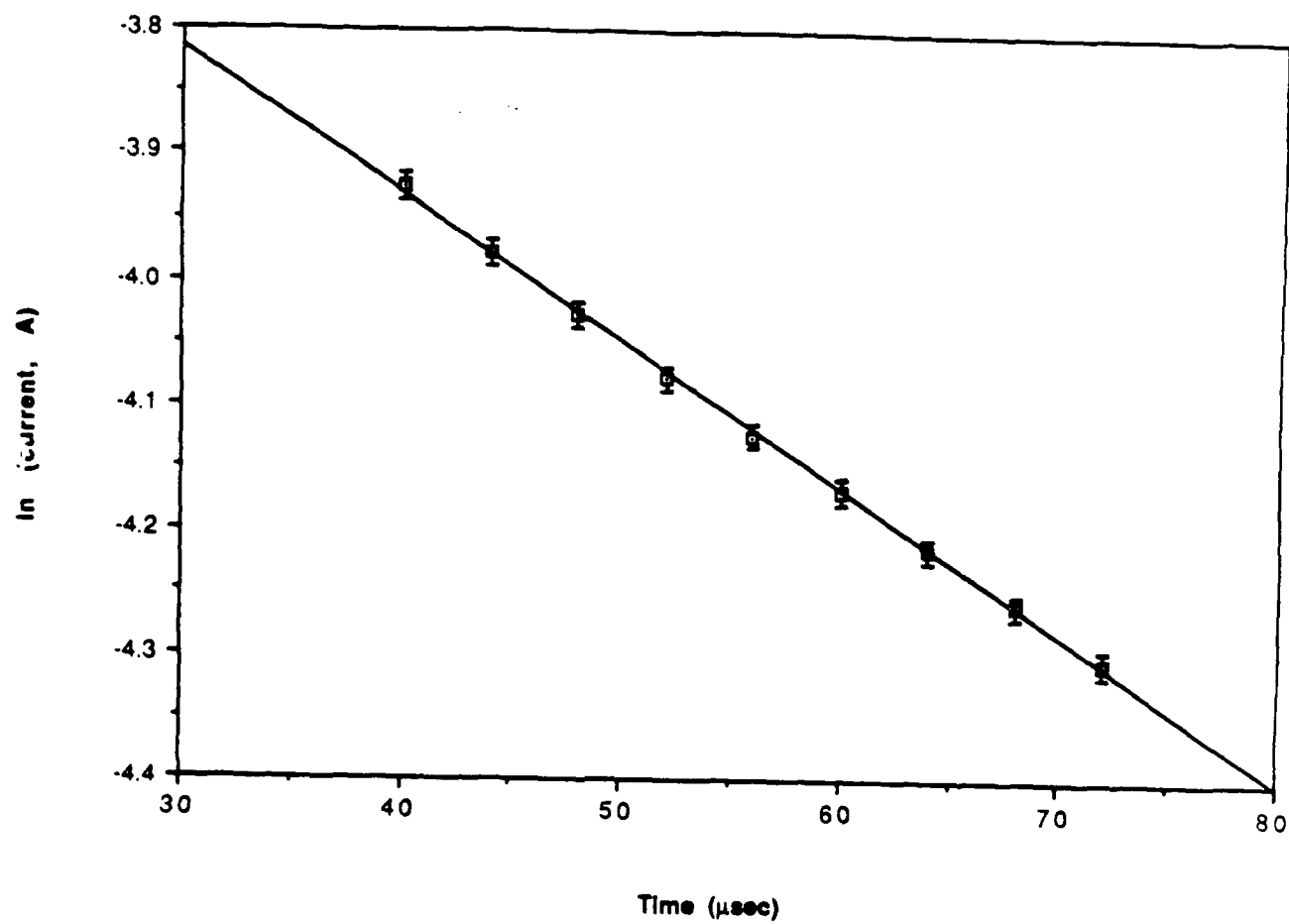


Fig 4

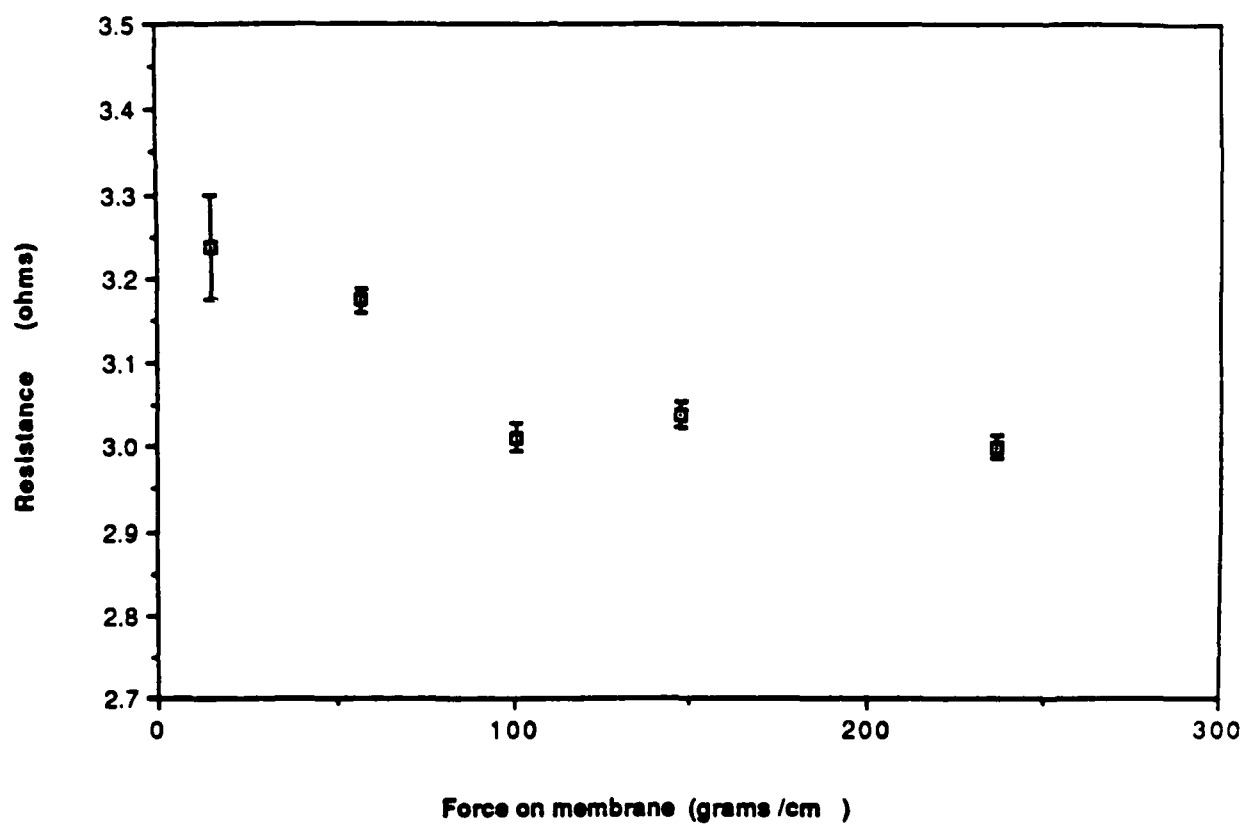


Fig 5

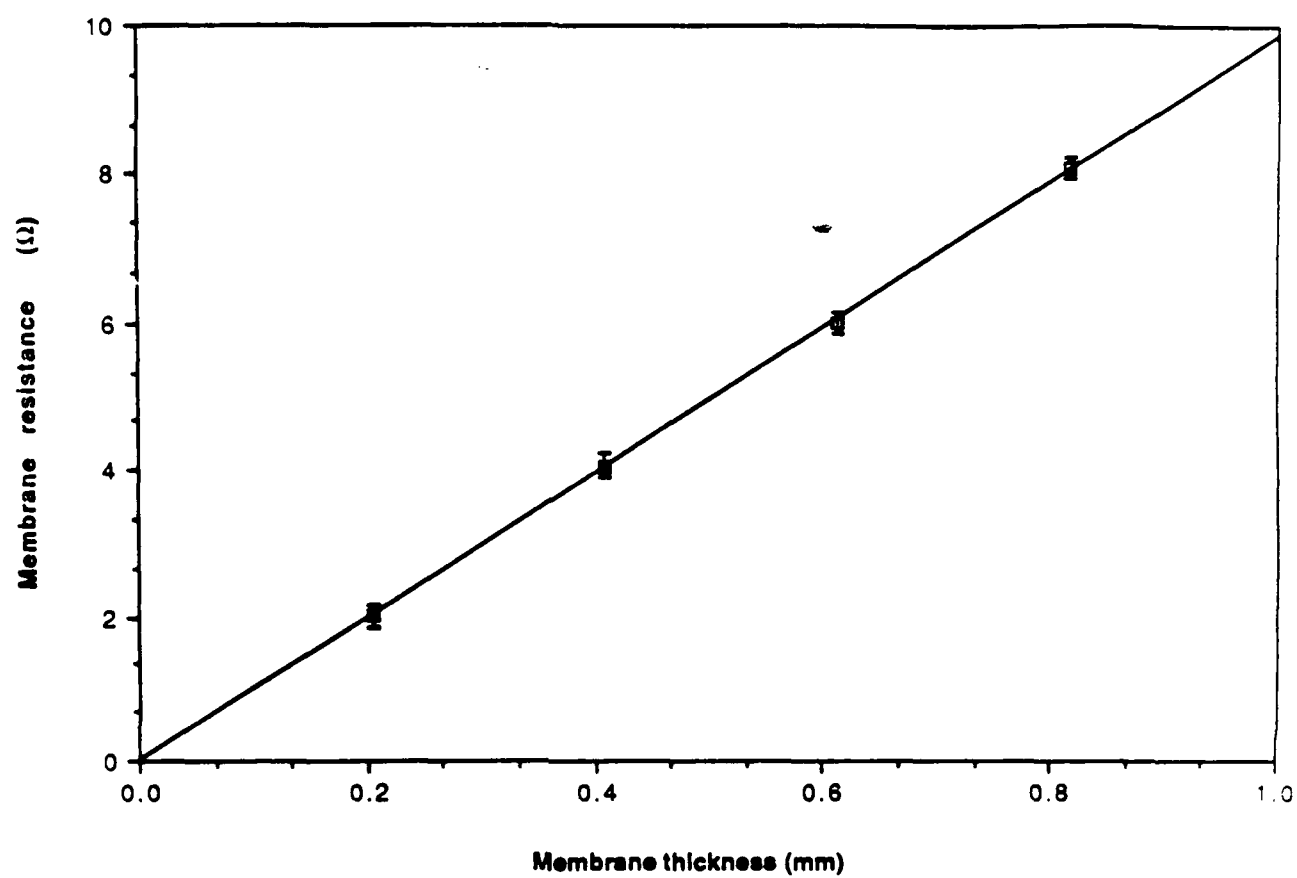


Fig 6

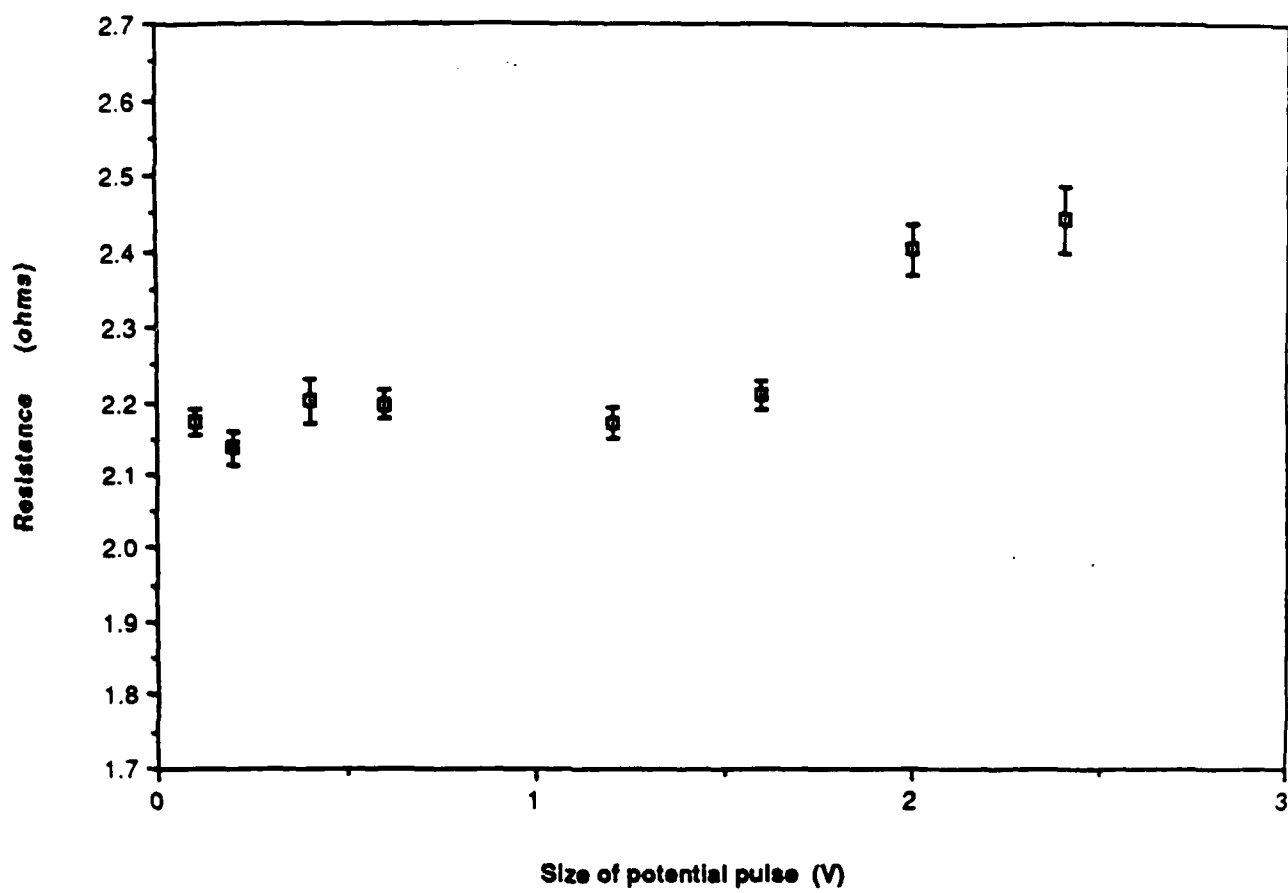


Fig 7

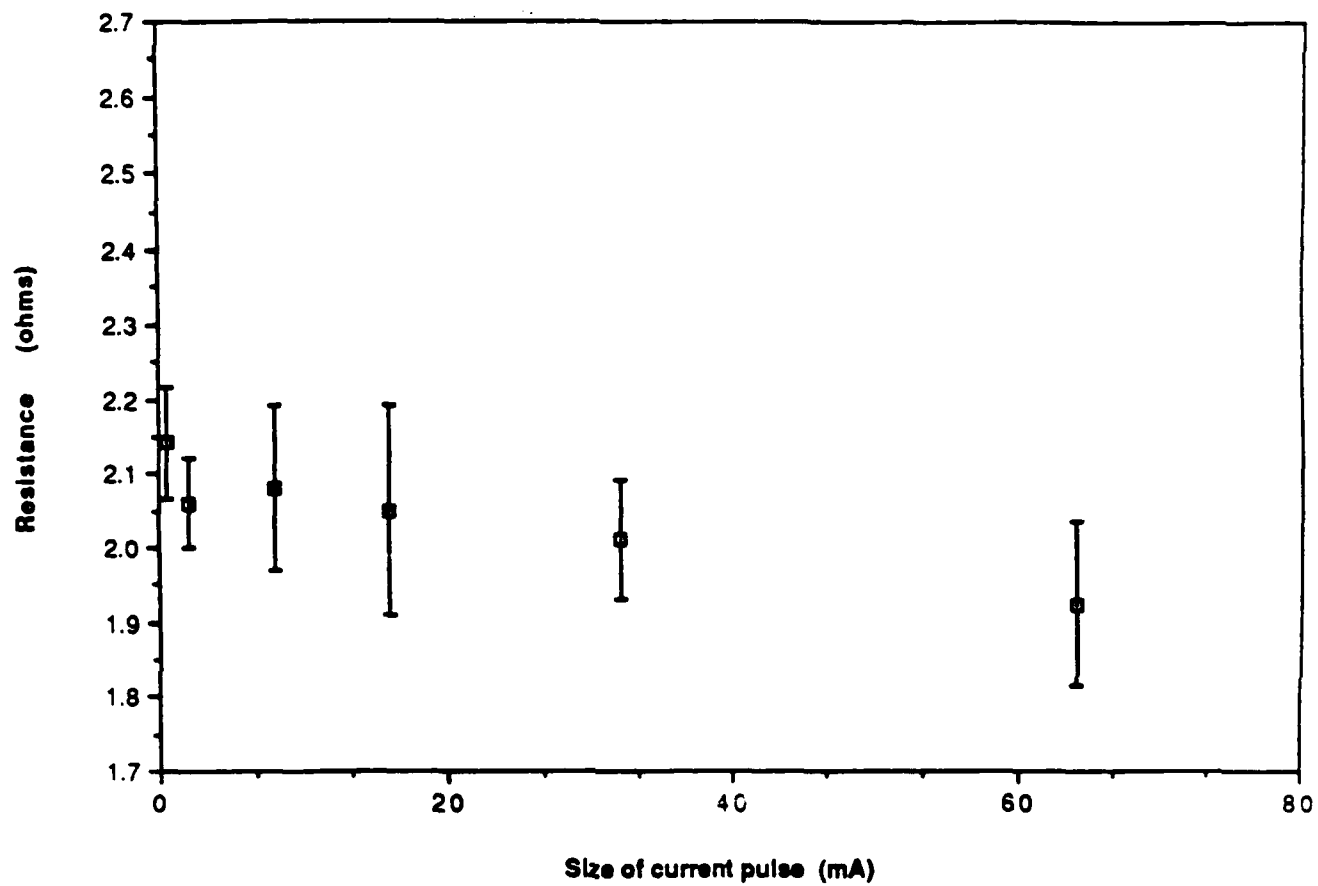


Fig 8

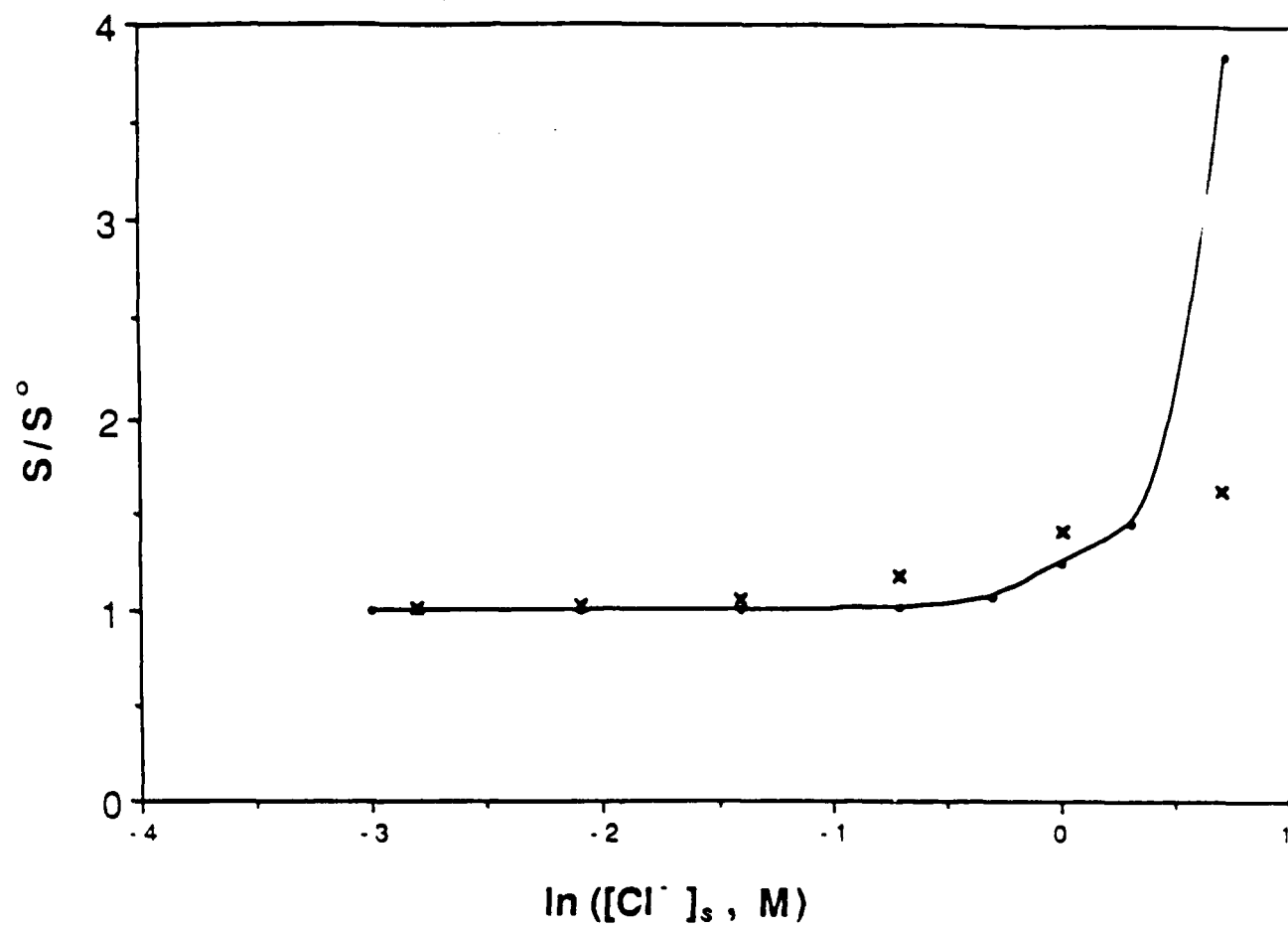


Fig. 1